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(54) Title: PROCESS FOR THE REMOVAL OF HYDROGENSULPHIDE (H_2S) FROM BIOGAS

(57) Abstract

A process for removing H_2S from biogas is provided, wherein the biogas is treated with an alkaline scrubbing liquid, the alkalinity necessary for absorption of H_2S originating from an aerobic biological waste water treatment plant. Thus, the water/biomass mixture form the aerobic treatment or the clarified effluent can be used as a scrubbing liquid. The water flow/gas flow ratio in the scrubbing process is preferably 0.2 or greater. The liquid wherein H_2S is absorbed can be recycled to the aerobic phase for oxidising the H_2S. The process can be performed using a closed column gas scrubber equipped with inlet and outlet for biogas, inlet and outlet for treated waste water and means for contacting biogas and waste water.

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PROCESS FOR THE REMOVAL OF HYDROGENSULPHIDE (H_2S) FROM BIOGAS

The invention relates to the removal of hydrogen sulphide (H_2S) from biogas.

Hydrogen sulphide is a disturbing but hardly avoidable component of biogas. A process frequently used for removing hydrogen sulphide from biogas is scrubbing the gas with an aqueous liquid having an increased pH. This increased pH can be adjusted by the addition of caustic soda or other agents. Such processes are known for example from European Patent Applications 229,587 and 331,806.

The efficiences that can be achieved with such processes vary from 50 to 99.9%, depending on the amount of hydroxide added and the capacity of the apparatus.

A drawback of scrubbers of the type is this high consumption of chemicals, resulting in high operational costs.

According to the present invention, the natural alkalinity generated during the aerobic biological purification of waste water is used instead of added alkaline chemicals (for example caustic soda).

Alkalinity is to be understood here as the total of negative ions and neutral particles that can dissociate H_2S.

This natural alkalinity can arise for example in the following two manners:

(a) Neutralized organic acids are converted into cell material and bicarbonate during the aerobic treatment, as follows:

$$R\text{-}COO^- + O_2 \rightarrow \text{cell material} + HCO_3^-$$

wherein R is for example an alkyl group, such as CH_3 or C_2H_5.

Carbon dioxide (CO_2) is stripped by aeration and the carbonic acid equilibria are shifted as follows:

$$H_2O + HCO_3^- \rightarrow OH^- + H_2CO_3 \rightarrow H_2O + CO_2 \uparrow \text{, or}$$

$$HCO_3^- \rightarrow OH^- + CO_2 \uparrow$$

This causes the pH to increase.

(b) Organic acids are removed during the aerobic treatment according to the equation:

$$CH_3COOH \rightarrow CH_4 + CO_2$$

This results in a marked pH increase.

By stripping carbon dioxide during the aerobic post-treatment as indicated at (a), the pH value increases further.

The aerobically treated waste water having alkalinity obtained in a natural way is contacted with the biogas containing H_2S. The waste

water may or may not contain biomass. The H_2S will be absorbed from the biogas into the aqueous phase.

The efficiencies that may be obtained in this way vary from 50 to 95%, depending on the water flow/gas flow ratio and the volume of the apparatus. For a H_2S removal rate of 50%, a water flow/gas flow ratio of 0.1 is generally sufficient. For higher efficiencies, a ratio of at least 0.2 and in particular 0.5 or higher can be chosen, depending on the composition of the waste water and the biogas.

As a result of the charge neutrality, the amount of natural alkalinity in the form of OH^- and HCO_3^- (in meq) generated during aerobic treatment is basically equal to the number of meq/l of cations (such as Na^+, K^+, Ca^{2+}, Mg^{2+}, etc.) present minus the number of free anions (such as Cl^-, SO_4^{2-}, etc.) present. Thus, a high salt concentration prior to the aerobic treatment can lead to an increased alkalinity after the aerobic treatment and CO_2 stripping.

The great advantage of the present process is that no added chemicals are used, causing the operational costs to be low. A further advantage is that scrubbing liquid containing the H_2S absorbed therein can be recycled to the aerobic treatment without difficulty and without further treatment. Another advantage is that the recycled washing liquid can serve to adjust the pH of the aerobic treatment, which may lead to further savings in chemicals.

The present process for removing H_2S from biogas can be used not only at the site where the waste water is treated both anaerobically and aerobically, but also where a sludge fermentation is present in addition to an aerobic plant.

Although biogas is most suitable to be stripped of H_2S, H_2S can in principle be removed from other gaseous effluents as well in this way.

The biogas formed in the anaerobic phase usually contains, in addition to methane and other gases, 0.1 - 3% by volume of H_2S and can be stripped of H_2S according to the invention by scrubbing it with aerobically treated water. Reactions including the following occur then:

$$H_2S \rightleftharpoons HS^- + H^+$$

$$H^+ + HCO_3^- \rightleftharpoons H_2O + CO_2$$

The water phase containing the H_2S absorbed therein is recycled to the aerobic phase, where a biological oxidation takes place according to the following equation:

$$H_2S + 2\,O_2 \rightarrow H_2SO_4$$

Two processes are preferred:

1. The aerobic effluent serving as scrubbing liquid can be taken from the aeration tank. In that case, the gas is scrubbed with a water/biomass mixture. This mixture containing absorbed H_2S is recycled to the aeration tank. Figure 1 depicts the liquid flows according to this embodiment in diagram form. Herein (1) represents the anaerobic treatment, (2) is the aeration tank, (3) is the secundary settling and (4) is the biogas scrubber.

2. Clarified effluent can also be used as a scrubbing liquid. In that case, the gas is scrubbed with water treated aerobically and containing a very low amount of biomass. The water containing absorbed H_2S is recycled to the aeration tank. Figure 2 depicts the liquid flows according to this embodiment in diagram form. The reference numbers have the same meanings as in figure 1. A disadvantage of this embodiment may be that the secundary settling tank has a higher hydraulic load.

An installation wherein the removal of H_2S from biogas according to the process of the present invention can be carried out is depicted in figure 3. In addition to an inlet 11 and an outlet 12 for biogas and an inlet 13 and an outlet 14 for scrubbing liquid, this installation comprises a contact material 15 for improving the H_2S transfer as well as a liquid collector 16.

Example

The process for removing H_2S from biogas has been tested in a purification plant treating waste water of a brewery.

The biogas produced in the anaerobic reactor was scrubbed with a water/biomass mixture originating from the aerobic (activated sludge) treatment of the carousel type.

Biogas data:

- Flow 150-225 m^3/hr
- H_2S concentration 0.2-0.4%
- CO_2 concentration 28-32%

Carousel data:

- Flow 250-350 m^3/hr
- pH 7.2-7.5
- Temperature 20-24°C

The results of the experiments are summarised in figure 4, wherein the percentage of H_2S removal in the biogas scrubber is plotted as a function of the water flow/gas flow ratio.

Claims

1. Process for removing H_2S from biogas by treating the gas with an alkaline liquid, characterised in that the alkalinity necessary for absorption of H_2S originates from an aerobic biological waste water treatment plant.

2. Process according to Claim 1, characterised in that the water/biomass mixture from the aerobic treatment is used as a scrubbing liquid.

3. Process according to Claim 1, characterised in that the clarified aerobic effluent is used as a scrubbing liquid.

4. Process according to any one of Claims 1-3, characterised in that a water flow/gas flow ratio of 0.2 or greater is used.

5. Process according to any one of Claims 1-3, characterised in that the liquid wherein H_2S is absorbed is subsequently recycled to the aerobic phase.

6. Gas scrubber suitable for carrying out the process according to any one of Claims 1-5, consisting of a closed column equipped with inlet and outlet means for biogas, inlet and outlet means for treated waste water and means for contacting biogas and waste water.

Fig - 1

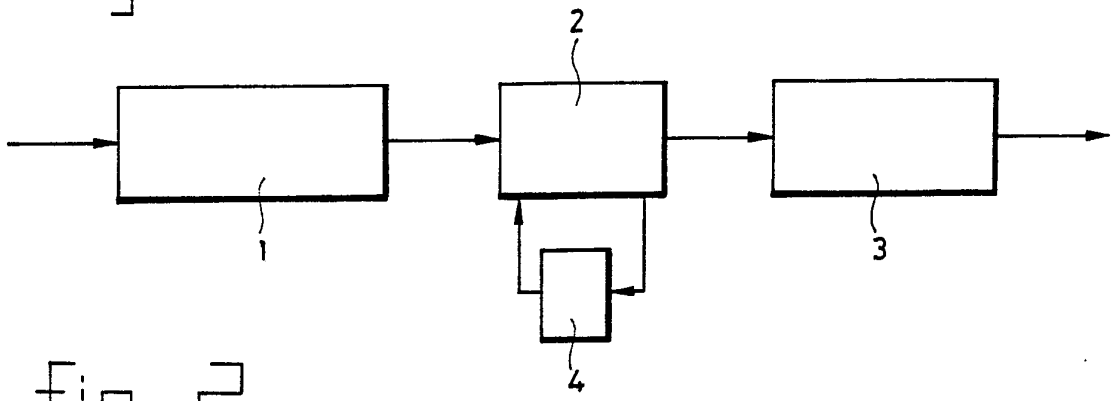


Fig - 2

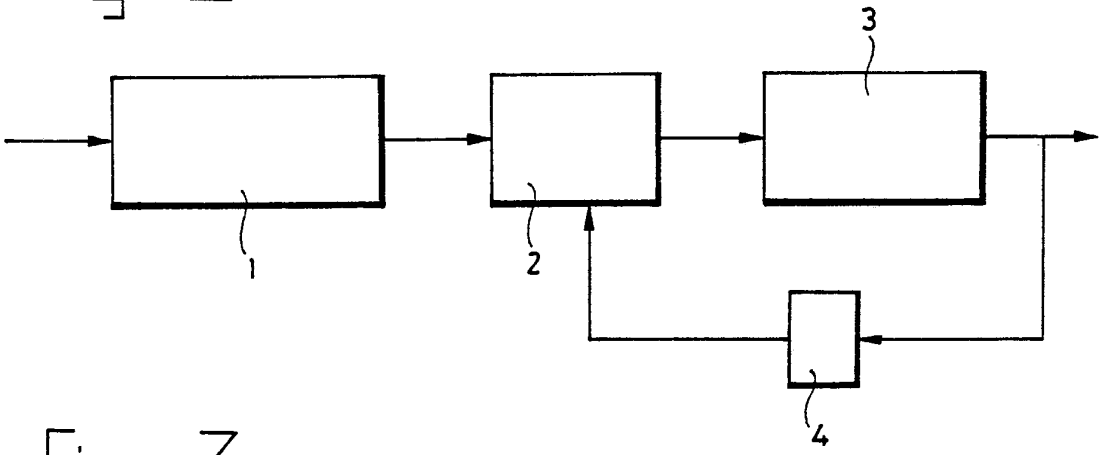


Fig - 3

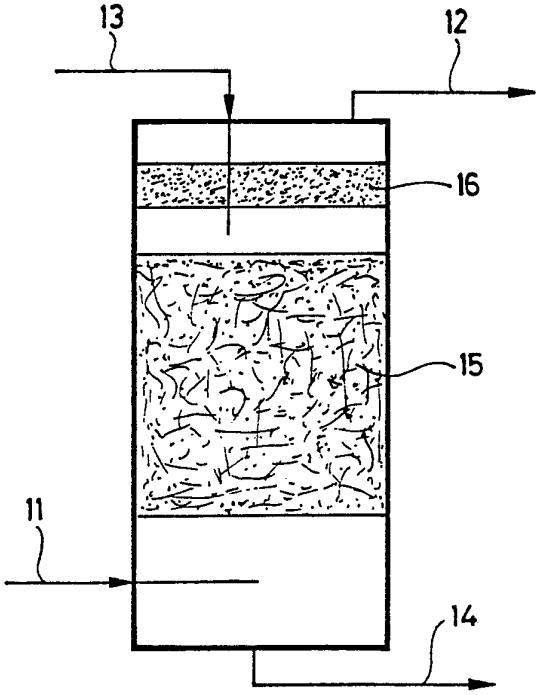
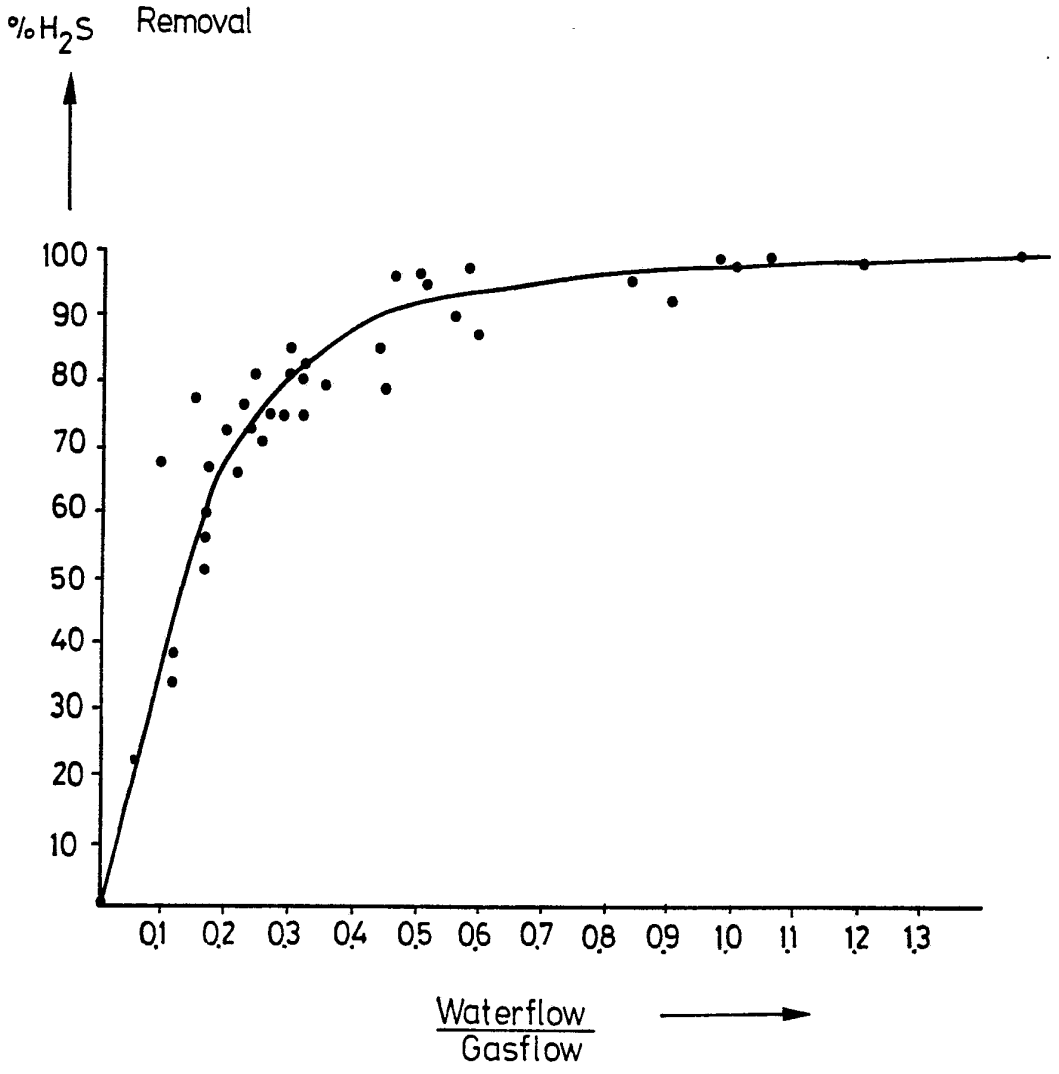


Fig-4


% H_2S Removal
100
90
80
70
60
50
40
30
20
10
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
Waterflow
Gasflow

INTERNATIONAL SEARCH REPORT

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International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

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II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	B01D ; C02F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	NL,A,8 602 150 (GRONTMIJ) March 16, 1988 see page 5, line 36 - page 7, line 20; figure 1 ---	1,2,5,6
A	DE,A,3 307 796 (LINDE) September 6, 1984 ---	
A	DE,A,3 423 285 (U. FUCHS) January 2, 1986 ---	
A	US,A,4 372 856 (J.R. MORRISON) February 8, 1983 ---	
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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
20 SEPTEMBER 1991	01. 10. 91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	BOGAERTS M.L.M.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

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DE-A-3307796	06-09-84	None	
DE-A-3423285	02-01-86	None	
US-A-4372856	08-02-83	None	
FR-A-2484990	24-12-81	FR-A- 2461684	06-02-81